TRANSLATION

GERMAN PRELIMINARY PUBLISHED APPLICATION NO. DE 3 734 764
A1
International Classification[4]: C 07 C 31/20
C 12 P 7/18
//(C12P 7/18,
C12R 1:22)

File No.: P 37 34 764.0

Date of filing: October 14, 1987. Date of disclosure: May 3, 1989.

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Title:
PROCESS FOR THE PRODUCTION OF 1,3-PROPANEDIOL

Abstract

In the fermentation of glycerol, known methods yield 1,3-propanediol in yields of up to about 60%.

According to the invention, the yield of 1,3-propanediol may be raised further by fermentation with the aid of the bacterial strain Klebsiella pneumoniae DSM 4270 in the presence of cobalt(II) salts.

Production of 1,3-propanediol.

The invention relates to a process for the production of 1,3-propanediol from renewable raw materials, using microorganisms.

Short-chain diols are important in industry and technology as structural units for polymers, solvents, and pharmaceuticals. They are constituents of adhesives, ointments, abrasives, lubricating oils, antifreezes, and brake fluids. 1,3-Propanediol has some fields of application that are significant in terms of quantity. These include the production of polyesters and polyurethanes and the synthesis of specific heterocyclic compounds.

Diethyl malonate may be hydrogenated to produce 1,3-propanediol.

Microbiological processes are also known for the production of 1,3-propanediol. Thus according to Mickelson and Werkmann, J. Bact. 39, 709 (1940), glycerol may be fermented by means of various Escherichia strains to produce 1,3-propanediol. The yield thereby is 30 to 60%. In Enzymologia 8, 252 (1940), the same authors describe the fermentation of glycerol to produce 1,3-propanediol with the aid of Aerobacter strains. The conversion of glycerol thereby to produce 1,3-propanediol is about 45%, with 2,3-butanediol also being formed as a by-product.

According to Forage and Foster, J. Bact. 149, 413 (1982), glycerol may be fermented by means of Klebsiella pneumoniae ATCC 8724 and 25 955 under anaerobic or aerobic conditions in a neutral or weakly alkaline medium to produce 1,3-propanediol. Acrolein is also formed thereby in significant amounts. The growth of the microorganisms may be stimulated here by vitamin B_{12}.

According to Forsberg, Applied and Environmental Microbiology 53, 639 (1987), glycerol may be converted into 1,3-propanediol with the aid of Chlostridium strains with the addition of cobalt chloride and cobalamin, whereby conversions of up to max 61% are achieved.

In the known processes for the production of 1,3-propanediol, conversions and yields of up to about 60% are achieved. By-products, primarily acrolein, are also formed thereby to quite a large extent and make the purification of the desired product more difficult.

It is the object of the present invention to prepare an improved process for the production of 1,3-propanediol. In particular, the yield and conversion are to be increased thereby.

The object is achieved according to the invention by fermenting glycerol by means of the microorganism Klebsiella pneumoniae DSM 4270 in the presence of fermentable carbohydrates and cobalt(II) salts under aerobic conditions.

Suitable carbohydrates are pentoses and hexoses such as for example arabinose, xylose, glucose, or mannose. It is preferable to use glucose.

The aqueous culture medium that is inoculated with the bacterial strain Klebsiella pneumoniae DSM 4270 initially contains 5 to 15% of glycerol and 2 to 10% of fermentable carbohydrates. The nutrient medium contains 0.01 to 100 μM cobalt(II) salts, for example cobalt(II) chloride. The content is preferably 0.05 to 10 μM.

The nutrient medium may additionally contain a complex organic nutrient source such as yeast extract, soybean peptone, or corn steep liquor. Purely synthetic nutrient solutions may also be fermented, however, that only contain inorganic salts in addition to the said substrates.

The fermentation of the glycerol is carried out aerobically, preferably under reduced aeration.

The temperature is held in a range of 25 to 35°C. Preferably a temperature of 30 to 33°C is established. During the conversion, the pH is held at 4 to 7. Preferably the mixture is adjusted to a pH of 4.5 to 6.

In the reaction, 2,3-butanediol is generally also formed as a by-product. By-product formation is influenced strongly by the fermentation conditions and depends primarily on the pH and the temperature.

Under the conditions of the invention, 60 to 82 g of 1,3-propanediol is formed from 100 g of glycerol, which corresponds to a maximum possible yield of 73 to 100%.

In carrying out the process, first a nutrient solution is used that contains glycerol as a carbon source. Then cobalt(II) salt is added, whereupon the solution is inoculated with an initial culture of Klebsiella pneumoniae DSM 4270. Hexoses or pentoses may be used together with glycerol. They may also be added only after fermentation has started, however.

With large batches, the fermentation broth is stirred under aerobic conditions. With small batches the fermentation is carried out while the reaction flask is shaken. The reaction is generally complete after 48 to 72 h.

When the conversion is complete, the cells are separated from the batch and the 1,3-propanediol is isolated in pure form by distillation and fractional distillation.

The 1,3-propanediol produced by the process of the invention is identified by its NMR spectrum and by its gas chromatographic behavior.

Example

4 L of culture medium that contains per liter

6.64 g	of K_2HPO_4
1.5 g	of KH_2PO_4
3.0 g	of $(NH_4)_2SO_4$
50.0 g	of glycerol
0.3 g	of $MgSO_4 \cdot 7\ H_2O$
0.1 g	of NaCl
0.058 g	of $CaCl_2 \cdot 2\ H_2O$
0.022 g	of $FeSO_4 \cdot 7\ H_2O$
0.003 g	of $MnSO_4 \cdot H_2O$
0.075 g	of $ZnSO_4 \cdot 7\ H_2O$
5.0 g	of yeast extract
2.5 μmol	of $CoCl_2$

is placed in a 5-L fermenter. This culture medium is sterilized and then inoculated with 40 mL of initial culture of the strain Klebsiella pneumoniae DSM 4270, whereupon the fermentation takes place under the following conditions:

pH 5.5
Temperature 30°C
Stirrer speed 300 rpm
Aeration with 0.15 vvm of air

After a fermentation time of 7 h, 50 g of glucose per liter is added to the fermentation broth. The fermentation is complete after 72 h.

After separation of the cells, analysis shows that 63 g of 1,3-propanediol has been formed per 100 g of decomposed glycerol.

If no glucose is added, only 38 g of 1,3-propanediol is synthesized per 100g of decomposed glycerol.

Patent Claims

1. Process for the production of 1,3-propanediol in high yields from glycerol using microorganisms, characterized in that glycerol is fermented with the aid of Klebsiella pneumoniae DSM 4270 in the presence of at least one pentose or hexose and of cobalt(II) salts under aerobic conditions.

2. Process according to Claim 1, characterized in that the fermentation is carried out in the presence of glucose.

3. Process according to Claim 1, characterized in that the fermentation is carried out in the presence of 0.01 to 100 μM cobalt(II) salts.

4. Process according to Claim 3, characterized in that the fermentation is carried out in the presence of 0.05 to 10 μM cobalt(II) chloride.

5. Process according to Claim 1, characterized in that the fermentation is carried out at 25 to 35°C in a pH range of 4 to 7.

6. Process according to Claim 5, characterized in that the fermentation is carried out at 30 to 33°C.

7. Process according to Claim 5, characterized in that the fermentation is carried out in a pH range of 4.5 to 6.

Transl.: Language Services
GRIFFITHS
August 31, 1994